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**Economic Comparison of  
UV/Oxidation, Anaerobic Fluidized Bed Reactor, and Granular Activated Carbon for the  
Treatment of Propellant Production Wastewater Containing 2,4-Dinitrotoluene**

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**Abstract**

2,4-Dinitrotoluene (2,4-DNT) is used in the manufacturing process of single- and multi-base propellants at the Radford Army Ammunition Plant (RAAP) in Radford, Virginia. Slug flows of 2,4-DNT enter the wastewater stream via discharge from several batch production operations including water-dry, wet screening, and solvent recovery. The existing biological wastewater treatment plant (BWTP) receives wastewater from all operations for treatment prior to discharge into the New River under a National Pollutant Discharge Elimination System (NPDES) permit. Previous studies have indicated that the BWTP influent wastewaters contain up to 75 mg/L of 2,4-DNT. The current daily discharge limits for 2,4-DNT are 113  $\mu\text{g/L}$  (average) and 285  $\mu\text{g/L}$  (peak). The BWTP has had occasional problems meeting this discharge level and it is anticipated that the discharge limit may be further reduced significantly.

To address this situation, the U.S. Army Environmental Center (USAEC) has conducted a pilot-scale field demonstration project at RAAP using a UV/Oxidation and an Anaerobic Fluidized Bed Bio-Reactor (AnFBR) for pre-treating the 2,4-DNT wastewater at the point of generation (i.e., upstream of the BWTP). During this demonstration, RAAP also implemented transportable Granular Activated Carbon (GAC) adsorbers as an interim measure to pretreat wastewater as it is generated from the solvent recovery and water-dry operations. The data collected during operation of these temporary carbon units has been compiled and analyzed with the UV/Oxidation and AnFBR systems. Treatment of these wastewaters is complicated by the presence of alcohol and ether in high concentrations. These solvents interfere with the treatment efficiency of UV/Oxidation and GAC in 2,4-DNT removal while assisting pre-treatment by AnFBR. These factors were investigated during the pilot tests and based on the experimental data, a preliminary design of full-scale units for each technology was established. A life-cycle economic cost analysis for each technology was then performed to compare the relative costs of each option and its economic return on investment.

This paper presents the conclusions of the pilot-scale demonstrations and a summary of the life-cycle cost comparison for the technologies evaluated.

## ***Introduction***

Recently, changes in production levels at the Radford Army Ammunition Plant (RAAP) coupled with increasingly stringent regulation of wastewater discharges, have resulted in the need for improved treatment of propellant production wastewaters containing 2,4-dinitrotoluene (2,4-DNT). The RAAP is a government owned, contractor operated (GOCO) facility currently operated by Alliant Techsystems, Inc. The RAAP produces a wide variety of propellants and explosives for use by the U.S. military. 2,4-DNT is used in the production of single-base propellants. This production process is conducted in a batch mode which includes operations which generate wastewater containing various concentrations of 2,4-DNT and other organics (e.g., ethanol and ether) and are discharged to the industrial sewer. An on-site biological wastewater treatment plant (BWTP) treats the combined flow of wastewater from most on-site production operations. The treated effluent is discharged from the BWTP to the New River which flows through the facility.

This discharge is regulated by the Commonwealth of Virginia under a National Pollutant Discharge Elimination System (NPDES) permit. It is anticipated that the state will significantly reduce the NPDES discharge limit for 2,4-DNT. Currently the daily discharge limits for 2,4-DNT are 113  $\mu\text{g/L}$  (average concentration) and 285  $\mu\text{g/L}$  (maximum concentration). In the past, the BWTP has occasionally discharged treated effluent that exceeded these concentrations but were within Virginia Water Quality Standards quantity limits for DNT in public water supplies based on the harmonic mean flow of the New River.

To support RAAP's efforts to address this situation, the USAEC sponsored an engineering study to identify the major sources of 2,4-DNT present in wastewater generated at RAAP, to characterize the flows and concentrations of these wastewaters, and conduct limited bench-scale testing of selected treatment technologies. This study concluded that the major contributor of 2,4-DNT load to the BWTP is the Water-Dry (WD) operation and recommended interception and treatment of WD wastewater prior to discharge from the WD tanks to the sewer to help ensure that the treated effluent from the BWTP is in compliance with the current and anticipated NPDES discharge limits for 2,4-DNT. Subsequently, the USAEC sponsored a follow-on study to demonstrate, at a pilot-scale, two treatment technologies. Ultraviolet Oxidation (UV/Oxidation) and Anaerobic Fluidized-bed Biological Reactor (AnFBR) with granular activated carbon technology were the two technologies selected for this pilot-scale demonstration based on the results of previous bench-scale work and other bench-scale work performed by USACERL. Additionally, a third technology, granular activated carbon (GAC) treatment was demonstrated at RAAP by Alliant Techsystems. The intent of these pilot-scale tests was to gather sufficient data regarding the treatment of 2,4-DNT in the wastewater that would allow scale-up to a full-scale system and perform an economic analysis to compare the costs of such systems.

## ***Pilot Test Results and Conclusions***

### ***UV/Oxidation***

A total of nine test runs were performed with the UV/Oxidation system. Four operating parameters were varied to evaluate performance of the UV/Oxidation system in terms of 2,4-DNT removal efficiency: retention time, ozone dosage, hydrogen peroxide dosage, and UV radiation intensity. The efficiency of UV/Oxidation treatment of 2,4-DNT in WD wastewater was found to

be largely dependent on the concentrations of ethanol and ether present in the wastewater. During the demonstration, this system was unable to reduce 2,4-DNT concentrations to the target limit (113  $\mu\text{g/L}$  2,4-DNT) except at very high oxidant dosages and extended residence times. However, the system consistently removed more than 65 percent of the 2,4-DNT in the wastewater. An evaluation of the flows to the BWTP is required to determine if this removal rate (i.e., 65 percent reduction) would permit the BWTP to meet anticipated discharge standards.

UV/Oxidation systems, in a wide variety of configurations to suit various process needs, are available through a number of commercial vendors. This technology has been implemented and proven effective and reliable on numerous wastewater streams. A relatively high degree of experience exists in the industry regarding the operation and maintenance of such systems.

### **AnFBR**

The demonstration of the AnFBR system was conducted between September 12, 1994 and July 26, 1995. During the demonstration the forward flow rate was on the order of 0.4 gpm to 2 gpm. The results of the AnFBR demonstration indicate that the system is capable of achieving the target effluent quality (i.e.,  $<0.113$  mg/L 2,4-DNT). Most of the tests conducted were performed at a relatively low flow rate of 0.4 gpm (i.e., retention time of 7.8 hours). The test runs that were performed at higher flow rates (up to 2 gpm) were run for shortened periods, due to the lack of WD wastewater. Additional testing at flow rates of 4 gpm or higher would enhance the evaluation of the system to achieve the required removal of 2,4-DNT.

AnFBR technology is currently available from a limited number of vendors. Compared with UV/Oxidation, AnFBR is an emerging technology. Because the degree of documented experience with AnFBR is less than with UV/Oxidation, it would likely be more difficult to start up and troubleshoot the AnFBR system. This was evidenced by startup problems experienced during the demonstrations. Operational upsets were encountered because of complications with the inflow pump, alcohol delivery pump, pH control solution pump, and the main control system. Additionally, level probes in the nutrient and hydrogen peroxide sampling tanks were problematic throughout the study. Although the system, as tested, was computer controlled, the system required significant operator attention. As is typical of biological systems, the AnFBR system required significant time for reacclimation following upsets which can be caused by variation in influent quality, temperature, and other variables.

### **GAC**

Subsequent to the demonstration of the UV/Oxidation and AnFBR systems, Alliant implemented the use of transportable Granular Activated Carbon (GAC) adsorbers as an interim measure to treat wastewaters generated from the SR and WD operations. This activity was implemented to reduce the 2,4-DNT load to the BWTP so that violations of the NPDES discharge limit for 2,4-DNT would not occur. The data collected during operation of these temporary carbon units was compiled and analyzed in a report submitted to USACERL. The information provided by Alliant is presented here to allow a comparative evaluation of GAC with AnFBR and UV/Oxidation.

The GAC units reduced the concentration of 2,4-DNT to an average of 0.02 mg/L in the effluent. This treated concentration is significantly less than the NPDES limit of 0.113 mg/L. The highest concentration of 2,4-DNT measured in the effluent (0.1 mg/L) also met the target discharge limit. During the time frame evaluated, a total of 260,000 gallons of SR and WD effluent were treated.

It is calculated that the GAC had adsorbed an estimated 51 lbs of 2,4-DNT. This amount is less than the projected capacity of the carbon (i.e., 72 lbs). Therefore, the holding capacity of the carbon was not exhausted during the study period.

The data indicate that the GAC initially adsorbed high levels of both alcohol and ether. These solvents were then desorbed when the influent concentrations dropped. This is evidenced by the fact that the observed concentrations of alcohol and ether in the effluent were frequently higher than the corresponding influent concentrations. However, the data does not indicate that 2,4-DNT or DAT adsorbed on the carbon was resolubilized during period of desorption of these solvents.

The system operated largely without problem. However, concerns existed regarding freezes that might occur during its use in winter months. A heater or heat jacket of some type would likely be required as a system modification to allow continual use of the GAC in sub-freezing temperatures.

### ***Design Basis for Full-Scale Systems***

Based on anticipated propellant production rates and WD cycle times, 4 gpm was selected as the flow rate design basis for a full-scale system. The design basis concentrations were selected based on the concentration levels of contaminants encountered during the pilot test demonstrations. These concentrations are: 2,4-DNT 100 mg/L average and 150 mg/L maximum; and, alcohol 300 mg/L average and 1,000 mg/L maximum. The treatment system could be expected to operate on an intermittent basis for a total of 175 days per year.

Using this design basis, the following full-scale systems were selected:

- UV/Oxidation - A system capable of providing a residence time of 960 minutes (reactor volume of 3,900 gallons), an ozone generator capable of providing 2,400 mg/L ozone, approximately 115 lbs/day ozone for a 4 gpm system, a hydrogen peroxide delivery system capable of delivering 200 mg/L (or about 9.5 lbs/day) hydrogen peroxide, total lamp power of 55 kW. The total electricity draw of the system would be about 81 kW (including the ozone generator).
- AnFBR - Two systems were considered for the full-scale application. One with a 5.2 m<sup>3</sup> bed volume. This system provides a safety factor of 3.5 based on 100 mg/L 2,4-DNT loading at 4 gpm. The other system considered has a 1.56 m<sup>3</sup> bed volume. This system does not provide a safety factor for treating 100 mg/L 2,4-DNT at 4 gpm.
- GAC - A system similar to that leased for temporary treatment was selected for the full-scale application. This system consists of two carbon adsorbers with total capacity of 3,600 lbs.

### ***Economic Comparison of Treatment Alternatives***

Cost estimates prepared for each of the three treatment alternatives evaluated in this study were calculated based on ten years of operation at 4,000,000 pounds of annual propellant manufacture and with an assumed interest rate of 7 percent. A graph showing the cumulative annual costs for ten years of operation is shown in Figure 1.

The costs calculated for the systems selected as potential candidates for full-scale application were as follows:

	UV/OX	1.56 m3 AnFBR	5.2 m3 AnFBR	GAC
Capital Cost	\$155,000	\$176,500	\$226,500	\$6,600*
Annual Operating Cost	\$22,300	\$10,900	\$14,250	\$80,500
Annual Operating Cost per 1,000 gallons	\$28	\$14	\$18	\$101
Present Worth (10 years at 7%)	\$311,400	\$252,900	\$326,500	\$571,800
Equivalent Uniform Annual Cost (10 years at 7%)	\$44,350	\$36,000	\$46,500	\$81,400

\* - Initial lease cost of the system

An analysis was performed to gauge the sensitivity of the economic analysis to the amount of propellant manufactured per year. A comparison of the cumulative operating costs over ten years for each alternative at annual propellant manufacture rates of 2,000,000 lbs and 6,000,000 lbs, respectively, is shown in Figures 2 and 3.

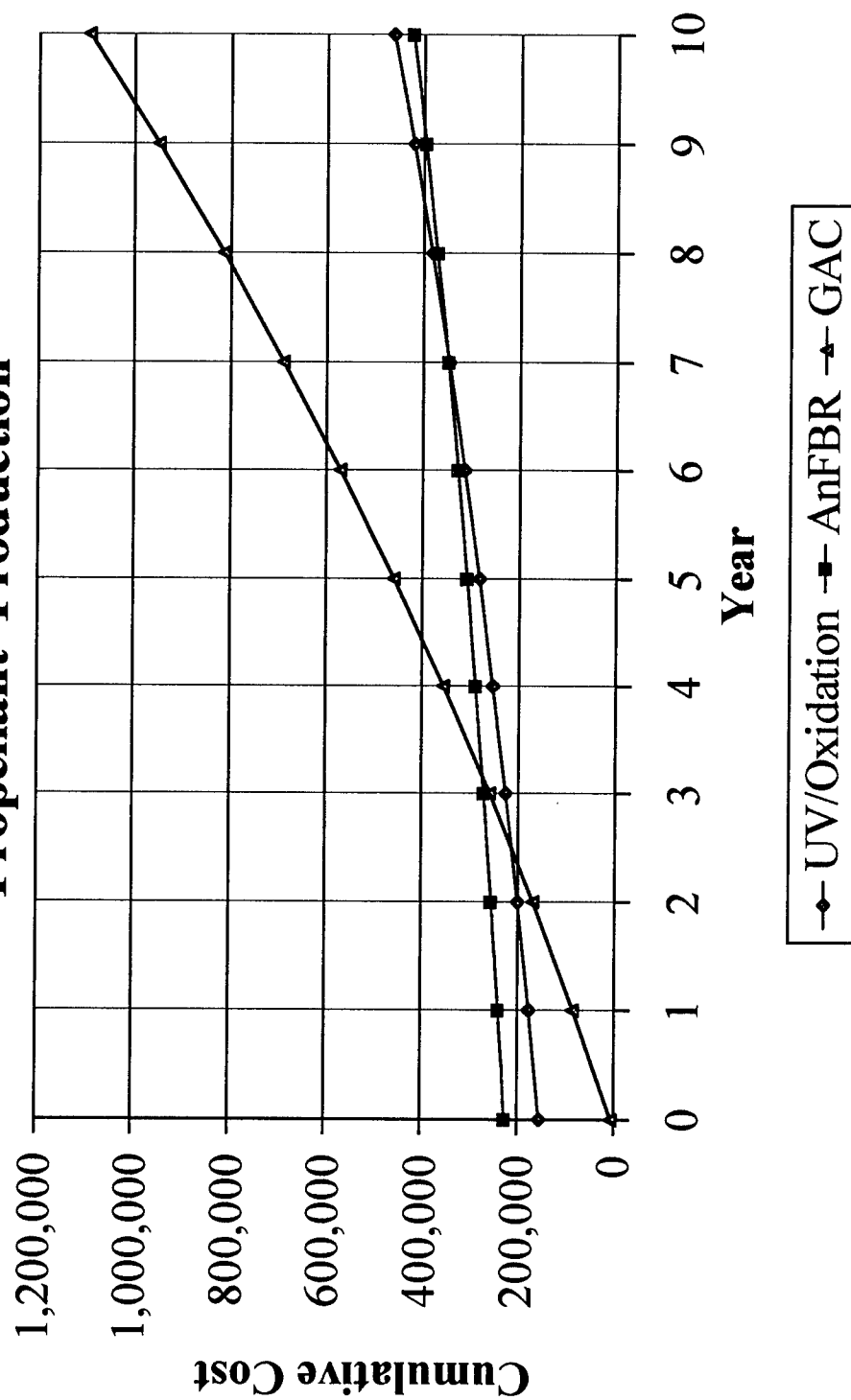
Based on the sensitivity analysis presented above, the selection of a system to be implemented at RAAP is dependent on both the amount of propellant likely to be manufactured per year and the length of time that manufacturing rate will be sustained. The difference in operating costs between the UV/Oxidation and AnFBR systems stem primarily from the number of expected operating days per year and is reflective of the fact that the UV/Oxidation system is capable of being shutdown for extended periods of time without the need for operator attention. Thus, the UV/Oxidation system is more cost effective for lower rates of propellant manufacture (i.e., lower volumes of wastewater generated per year). The AnFBR system requires continuous operator attention even in periods when WD wastewater is not generated. Furthermore, the AnFBR system must be fed supplemental alcohol during periods when wastewater is not available to maintain a viable microbial population in the reactor. Thus, increased propellant manufacture rates (and, hence, increased wastewater volumes generated) favor the economics of operation for the AnFBR system.

### **Conclusions**

- All three technologies were shown to be capable of treating 2,4-DNT to the desired effluent levels.
- UV/Oxidation is well suited for treatment of intermittent flows. The system can be shut down and restarted quickly and as required. UV/Oxidation was the most susceptible to changing alcohol levels.
- GAC is a proven and readily implementable technology. It has been demonstrated to be effective in removing 2,4-DNT from WD wastewater at RAAP.
- The AnFBR system required significantly more effort to set up and operate than the UV/Oxidation system. An acclimation period is required at start-up or after significant changes or upsets in operating conditions.

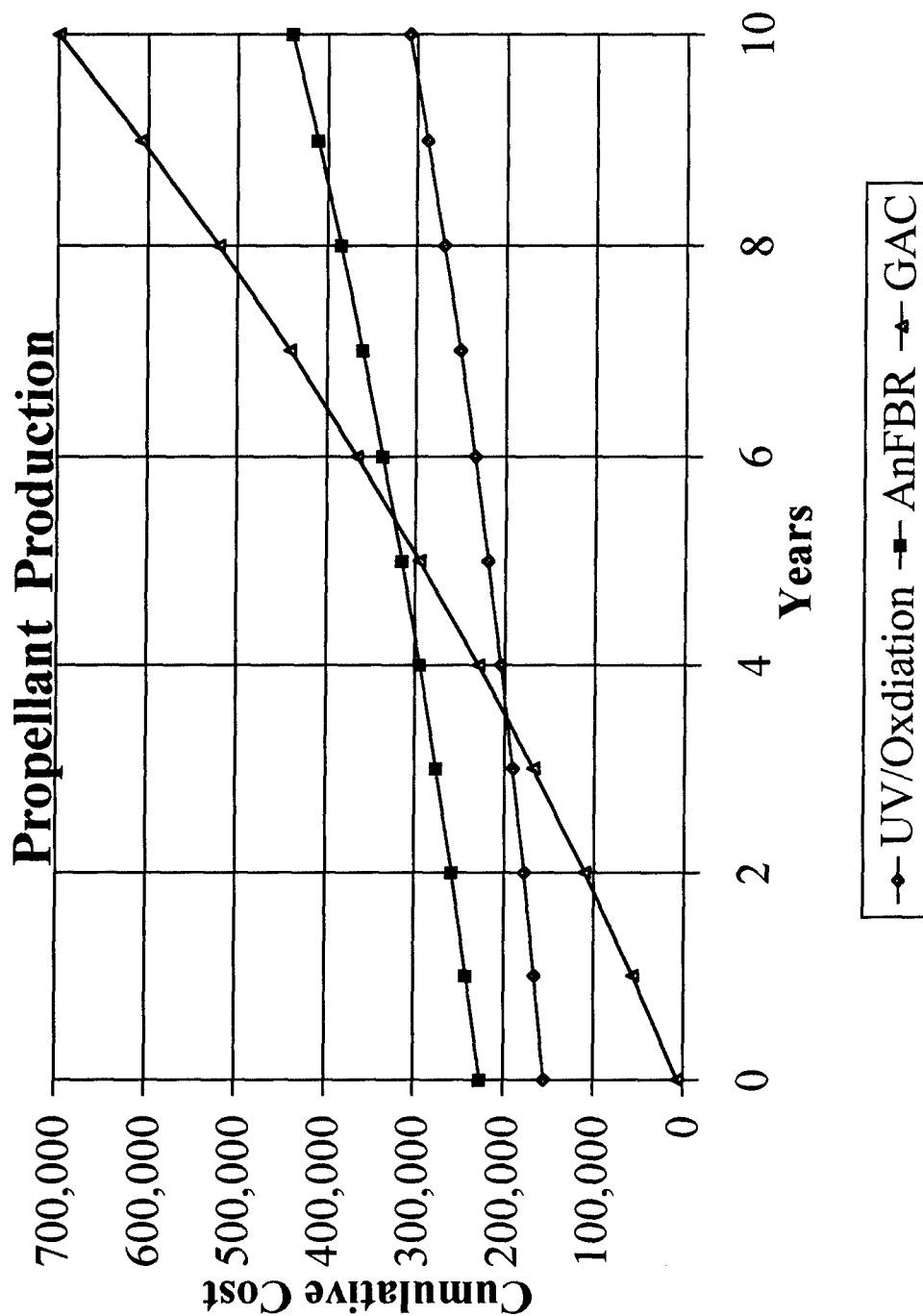
- The AnFBR consistently reduced concentrations of 2,4-DNT to levels below the target of 0.113 mg/L.
- An AnFBR system would have to be operated continuously to maintain a viable biomass and to avoid lengthy start-up times.
- GAC system has the lowest cumulative costs for the first 2 to 3 years of operation when compared to UV/Oxidation and AnFBR.
- Changes in the concentration of 2,4-DNT present in WD wastewater significantly impact the cost of treatment by GAC.
- Over longer periods, UV/Oxidation is estimated to be the most cost effective alternative at low propellant production rates and AnFBR is more cost effective at current and higher production rates.

**Figure 1**  
**Ten-Year Costs Based on 4,000,000 lbs of**  
**Propellant Production**





**Figure 2**  
**Ten-Year Costs Based on 2,000,000 lbs of**



**Figure 3**  
**Ten-Year Costs Based on 6,000,000 lbs of**  
**Propellant Production**

